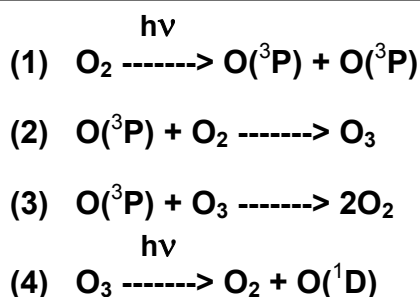# 2 Photochemistry Background

A brief review of photochemistry related to ozone formation is given here to minimize repetition that would otherwise be necessary in Chapter 3.

With very limited exceptions, ozone is not directly emitted by pollution sources. Rather, ozone is formed in the atmosphere through a complex set of chemical reactions initiated by ultraviolet sunlight. These chemical reactions chiefly involve volatile organic compounds (VOCs) and oxides of nitrogen, chiefly nitric oxide (NO) and nitrogen dioxide (NO_2), together referred to as NO_X.

Without VOCs and NO_X from human activities, ozone concentrations near the surface of the earth would be limited to approximately 15-20 parts per billion (ppb). When anthropogenic VOCs and NO_X are present, however, ozone concentrations can reach levels that compromise human health. State and federal standards for ozone (averaged over one hour) indicate that exposure to concentrations as low as 90 to 120 ppb can adversely affect lung function. If exposure to ozone lasts 8 hours or longer, average concentrations as low as 80 ppb can have an adverse impact.

Composed of three oxygen atoms, ozone (O_3) is a stable but highly reactive molecule.[1] During the 1800s, ozone was discovered and its presence detected in the upper atmosphere (altitudes above approx. 12 km). The formation of ozone in the upper atmosphere was explained in 1930 as a chemical process involving radiant energy ($h\nu$) from the sun. Certain wavelengths in the ultraviolet range are able to break oxygen (O_2) into two low-energy oxygen atoms, each denoted $O(^3P)$. Each free oxygen atom can combine with an oxygen molecule to form ozone. Ozone can also be removed by combining with an oxygen atom or by photolysis that generates a high-energy oxygen atom, $O(^1D)$. The equations below show these processes:

$$\text{(1)} \quad O_2 \xrightarrow{\;h\nu\;} O(^3P) + O(^3P)$$

$$\text{(2)} \quad O(^3P) + O_2 \longrightarrow O_3$$

$$\text{(3)} \quad O(^3P) + O_3 \longrightarrow 2O_2$$

$$\text{(4)} \quad O_3 \xrightarrow{\;h\nu\;} O_2 + O(^1D)$$

Reaction (1) is limited to the upper atmosphere due to the complete absorption of those wavelengths of sunlight by the atmosphere. Sufficiently energetic wavelengths of sunlight penetrate the troposphere and allow reaction (4) to occur throughout the atmosphere.

[1] The following discussion of ozone photochemistry was adapted from materials prepared by Dr. H. Jeffries (see references).
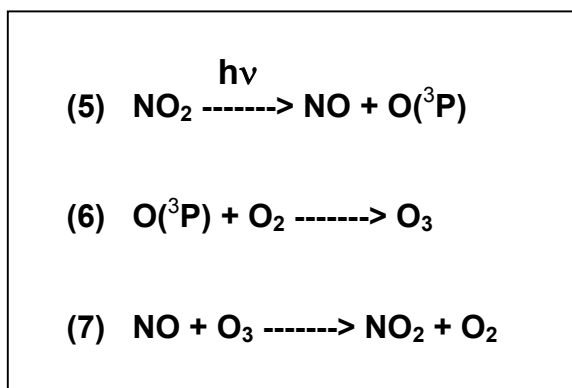
Natural exchange between the lower atmosphere and the ozone layer in the upper atmosphere produces a natural background level of ozone at the earth's surface of about 15-20 ppb. However, much higher levels of ozone are detected routinely at the earth's surface in areas affected by pollutants produced by human activity. Although some natural processes, such as lightning, can generate ozone, they cannot account for most instances of high ozone levels in urban areas. Instead, a series of reactions involving common pollutants was shown to govern ozone in the lower atmosphere.

First, radiant energy with a wavelength of 430 nm was shown to break nitrogen dioxide (NO_2) into NO and $O(^3P)$. Then, reaction (2) can proceed to form ozone. The ozone that forms, however, can react quickly with NO to produce NO_2 and O_2. The box below contains these three reactions repeating (2) above as (6).

The importance of NO_2 photolysis is illustrated by an interesting observation. When VOCs are weighted by their ozone-forming potential (reactivity), ozone concentrations in very different environments are strongly correlated with NO_X concentrations but only slightly correlated with VOC concentrations (Seinfeld & Pandis, 1998; Chameides, 1992; National Research Council, 1991).

Human activity produces rather little NO_2 directly, but fuel combustion that produces temperatures above 2000 ^oC can cause nitrogen (N_2) and oxygen (O_2) to combine and produce two molecules of nitric oxide (NO). Of course, reaction (7) could then convert the NO to NO_2, but ozone would be destroyed, not created, in the process.

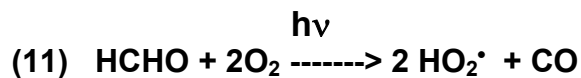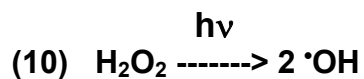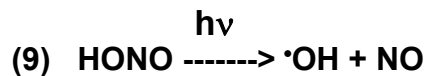Near the earth's surface, reaction (5) is the only significant source known for the
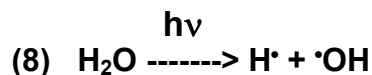
$$(5) \quad NO_2 \xrightarrow{\quad h\nu \quad} NO + O(^3P)$$

$$(6) \quad O(^3P) + O_2 \longrightarrow O_3$$

$$(7) \quad NO + O_3 \longrightarrow NO_2 + O_2$$

low energy oxygen atom, $O(^3P)$, needed to form ozone. The cycle of reactions (5), (6), and (7) first generates and then destroys ozone. In the lower atmosphere, net ozone production would be very limited unless there is a process for turning NO into NO_2 without destroying ozone at the same time. This is where VOCs participate in ozone formation. They play a central role in processes by which "free radicals" convert NO into NO_2 without destroying ozone.
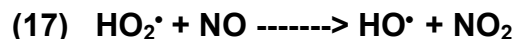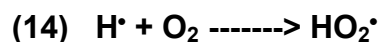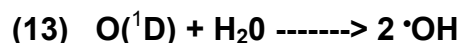
Molecules known as "free radicals" were well-known phenomena in combustion chemistry, but their relationship to urban smog did not emerge until after room-temperature reactions between hydroxyl radicals and hydrocarbons (VOCs) were demonstrated in 1967. A free radical is a highly reactive atom or molecule that has an unshared electron ready to be shared with another atom or molecule. Unlike ions that carry an electric charge, radicals have no charge because they have an equal numbers of protons and electrons.

Radicals in the atmosphere are produced through reactions that involve high-energy solar radiation that splits molecules, a process called "photolysis." Reactions (1), (4), and (5) above are examples of photolysis. More photolytic reactions that generate radicals are given in the box below. In these reactions, the symbol "•" indicates the unshared electron that characterizes a radical.

Additional reactions can propagate radicals or even increase the number of radicals. A radical propagates when it takes one radical type and produces another radical type. A reaction multiplies the number of radicals when more radicals exist

$$
\begin{array}{l}
\qquad\qquad h\nu \\
(8) \quad H_2O \text{ ------->} H^\bullet + {}^\bullet OH \\[1em]
\qquad\qquad\quad h\nu \\
(9) \quad HONO \text{ ------->} {}^\bullet OH + NO \\[1em]
\qquad\qquad\quad h\nu \\
(10) \quad H_2O_2 \text{ ------->} 2\ {}^\bullet OH \\[1em]
\qquad\qquad\qquad h\nu \\
(11) \quad HCHO + 2O_2 \text{ ------->} 2\ HO_2^\bullet + CO \\[1em]
\qquad\qquad\qquad\quad h\nu \\
(12) \quad CH_3CHO + 2O_2 \text{ ------->} CH_3O_2^\bullet + HO_2^\bullet + CO
\end{array}
$$
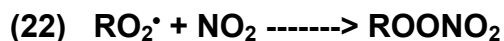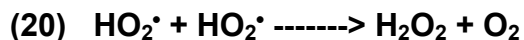
after the reaction than before. The reactions in the box below propagate radicals, and some also increase the number of radicals.

(13) $O(^1D) + H_2O \text{ -------> } 2\ ^\bullet OH$

(14) $H^\bullet + O_2 \text{ -------> } HO_2^\bullet$

(15) $OH^\bullet + R \text{ -------> } R^\bullet + H_2O$

(16) $RO^\bullet + O_2 \text{ -------> } R'CH + HO_2^\bullet$

(17) $HO_2^\bullet + NO \text{ -------> } HO^\bullet + NO_2$

(18) $RO_2^\bullet + NO \text{ -------> } RO^\bullet + NO_2$

In these reactions, R and R' are hydrocarbons (a class of VOCs)

Reaction (17) and reaction (18) indicate how NO can be converted to NO_2 in the atmosphere without losing ozone (O_3) in the process. The NO_2 can then initiate the production of more radicals through the photolysis in reaction (5).

Radical-terminating reactions are another important type of reaction in the photochemical system. The reactions in the following box remove radicals (at least temporarily) from the photochemical system.

(19) $NO_2 + {}^\bullet OH \text{ -------> } HNO_3$

(20) $HO_2^\bullet + HO_2^\bullet \text{ -------> } H_2O_2 + O_2$

(21) $RO_2^\bullet + NO \text{ -------> } RONO_2$

(22) $RO_2^\bullet + NO_2 \text{ -------> } ROONO_2$

In reaction (19), reaction (21), and reaction (22), NO or NO_2 combines with a radical to produce a product that is not a radical, thus terminating a radical propagation chain. Through photolysis or through thermal decomposition, the products of the radical terminating reactions above may be reversed, recreating their original ingredients. Reaction (19) was once thought to be a permanent sink for NO_x and for radicals. Recently, however, scientists have found that nitric acid (HNO_3) on surfaces can react with NO to regenerate NO_2. This may increase the ozone-forming potential of NO_X emissions.

In the collection of reactions (1 through 22) above, NO_x participates in processes that create radicals and in processes that terminate radicals. In a given air parcel, the relative balance of VOCs and NO_X (including their reaction products) helps determine whether the available NO_X behaves as a net ozone generator or a net ozone inhibitor.

The balance between VOCs and NO_X is commonly expressed in terms of the VOC/NO_X ratio. When the VOC/NO_X ratio is low (approx. 8 ppbC/ppb or lower), NO_X is plentiful relative to VOC and NO_X is likely to be a net ozone inhibitor. In such cases, the amount of VOCs tends to limit the amount of ozone formed, and we say that ozone formation is "VOC-limited" or "VOC-sensitive."

When the VOC/NO_X ratio is high (approx. 10 ppbC/ppb or higher), VOC is plentiful relative to NO_X, and NO_X is likely to be a net ozone generator. In such cases, the amount of NO_X tends to limit the amount of ozone formed, and we say that ozone formation is "NO_X-limited" or "NO_X-sensitive."

These properties are exhibited in the Empirical Kinetics Modeling Approach (EKMA), a simple system initially developed more than twenty-five years ago to estimate the response of ozone to changes in VOCs and/or NO_x. An EKMA diagram is shown in Chapter 3 (Figure 3-1). In this version of an EKMA plot, the VOC to NO_X ratio that produces the maximum ozone concentration is about 8 ppbC/ppb.

As the EKMA diagram shows, the effect of the VOC/NO_X ratio is not the same in all circumstances. Furthermore, the shape of the EKMA diagram is not the same at every site. The effect of the VOC/NO_X ratio may vary for the following reasons among others:

- The ratio that produces the highest ozone depends in part on the mix of VOC species, which may differ in their reactive properties.
- The reactivity of VOCs may decrease as NO_X decreases. Therefore, an increase in the VOC/NO_X ratio when emissions are high may lead to a greater proportional increase in ozone compared to the same increase in the VOC/NO_X ratio when emissions are lower (Carter, 1995).
- The VOC/NO_X ratio can differ substantially by location and time-of-day within a geographic area (Seinfeld and Pandis, 1998; Finlayson-Pitts and Pitts, 2000).

The VOC/NO_X ratio typically increases during the day. This happens in part because hydroxyl radicals react more rapidly with NO_2 than they do with VOCs. This causes NO_x to be removed from the photochemical system at a faster rate compared to VOCs. The denominator decreases faster than the numerator, so the ratio increases. In some cases, VOC-limited conditions can become NO_x-limited as air is transported away from sources of fresh emissions – either horizontally to downwind areas or vertically into the air hundreds of meters above the ground. In a VOC-limited air mass, an increase in the rate of ozone formation due to increasing VOC/NO_X ratios during transport may be offset by dilution in the absence of fresh

emissions.   Further complexity is introduced when an air mass moves over sources of fresh VOC and NO_x emissions.

Although this discussion has been limited to very general principles regarding photochemistry and ozone formation, it provides an adequate foundation for discussing the alternative causes for the ozone weekend effect offered as hypotheses in the following chapter.

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